EARTH'S WATER ADDED DURING LATE-STAGE PRIMARY ACCRETION? K. R. Bermingham[1] and R. J. Walker[1]. [1]Department of Geology, University of Maryland, College Park, Maryland, 20742, USA, (kberming@umd.edu).

Introduction When was water was delivered to Earth? Perspectives on this vigorously debated topic can be distilled into essentially three hypotheses. The "wet scenario" in which water and organics were delivered to Earth by the primary building blocks during main-stage accretion [e.g., 1]. This scenario requires that portions of material added during main-stage accretion originated sufficiently far from the sun so as to preserve water and organic material. The "dry scenario" purports that main-stage accretion was dominated by dry material likely originating from the inner solar system [2], and water/organics were added principally during late accretion (post-final core segregation). And, the "nebular ingassing scenario", where a portion of Earth's water came from the dissolution of nebular hydrogen into early Earth magma oceans during accretion [e.g., 3].

Approach One way to distinguish between these scenarios is by employing isotopic tracers which (1) discriminate between likely inner *vs.* outer Solar System materials, and (2) were accreted to Earth during different stages of its evolution.

Solar nebular isotopic tracers: Siderophile (Ni, Mo, Ru, W) elements possess nucleosynthetic isotope anomalies which likely formed from the heterogeneous distribution of presolar grains throughout the nebula [4-10]. These mass-independent isotope variations permit the classification of meteorites into the "non-carbonaceous" (NC) and "carbonaceous chondrite" (CC) groups [4, 7-10]. Based on highly anomalous Mo isotope compositions of carbonaceous chondrites and some iron meteorites, [6] proposed that CC parent bodies formed outboard of proto-Jupiter and were enriched in water and organics compared to NC parent bodies.

Isotopic tracers of terrestrial accretion: Moderately siderophile element Mo and highly siderophile element (HSE) Ru can provide constraints on Earth's late-stage primary accretion and late accretionary history, respectively. The Mo isotope compositions of the bulk silicate Earth (BSE) was likely established during high pressure/temperature metal-silicate partitioning [11,12]. Consequently, the final 10 to 20 % of mass accreted to Earth likely established ~90 % of the Mo in the BSE [13]. To date, high pressure metal-silicate experiments have not reproduced key characteristics of HSEs in the BSE in concert. An alternative mechanism to establish their abundances in the silicate Earth is so-called "late accretion" via the addition the final 0.5 to 2 wt.% of Earth's mass post core formation, by material with bulk chondritic HSE compositions [14-17].

The Mo-Ru cosmic correlation: This correlation, first identified by [13] and later refined by [5,10], indicates that Mo and Ru nucleosynthetic isotope anomalies in meteorites co-vary due to the variable distribution of *s*-process material in the nebula. Importantly, it has been considered that BSE lies on the correlation, signifying there was no major change in the genetic compositions of Earth's accretionary components throughout late-stage accretion, including late accretion [13]. The BSE composition, however, has been constrained using plasma standards [5,13] which may not provide represent BSE.

Methods To provide a more robustly defined Mo-Ru signature of the BSE, we compile previously published [10,18] and add new data for 26 mantle or mantle-derived terrestrial samples. Samples were obtained from around the globe and range in age from Archean to modern (**Table 1**).

Table 1. Samples analyzed in this study.

Sample type	Analyzed for Mo	Analyzed for Ru	~ Age
Chromitites	X	√	495 Ma
Os-Ir-Ru alloys	X	√	3.1 Ga to 80 Ma
Molybdenites	√	X	200 to 25 Ma
Diamictites	√	X	2.9 Ga to 0.3 Ma
OIBs	√	X	Modern

Results and Discussion The Mo and Ru isotope compositions of the samples are identical to the *Alfa Aesar* plasma standards used in our laboratory, within the measurement uncertainties (2SD). The compositional similarity between samples indicates a generally well-mixed mantle from which a composite estimate of the BSE composition can be made: μ^{97}Mo +3±2 (2SE) and μ^{100}Ru +1±2 (2SE)[10,18]. The BSE composition is indistinguishable from NC group iron meteorites (IAB main group and sLL subgroup) and is most disparate in composition to members of the CC group, which form a discreet cluster on the correlation [10,18]. This BSE composition plots within uncertainty of the μ^{97}Mo *vs.* μ^{100}Ru cosmic correlation as defined by *s*-process dominated isotopes, indicating that there was no major change in material accreted to Earth during late-stage accretion.

The μ^{94}Mo (*p*-process) *vs.* μ^{95}Mo (*r*-, *s*-process) isotopes are useful when considering potential *r*- and *p*-process contributions to the BSE. Here, we consider only iron meteorites to define the NC and CC parent body compositions. This is to avoid the effects of parent body alteration which can substantially modify isotope composition on the sampling scale [19] and consequently lead to a misrepresentation of a parent body siderophile element isotope composition [10].

The NC and CC groups are well-discriminated on this plot: NC iron meteorites fall along an *s*-process mixing line and CC iron meteorites form a discreet cluster plotting above the NC *s*-process correlation (**Fig. 2**)[7-9]. Addition of some isotopically unique meteorites (IIC irons, Wiley) may define a CC trend, but it currently remains unknown whether these meteorites are of the CC genetic type.

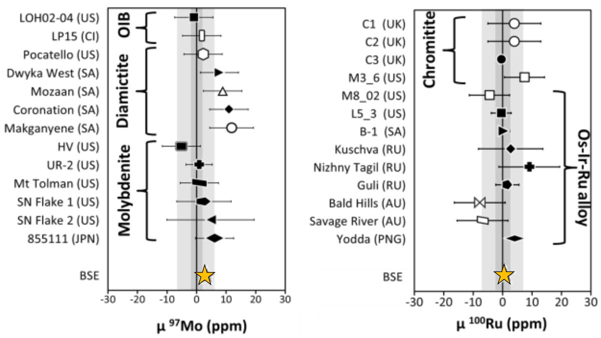

Fig. 1. μ^{97}Mo and μ^{100}Ru isotope compositions of terrestrial samples reported here (where μ refers to the parts per million deviation of the sample composition from the *Alfa Aesar* plasma Mo or Ru standard).

The sample derived BSE composition plots above the μ^{94}Mo *vs.* μ^{95}Mo linear regression defined by NC-iron meteorites (**Fig. 2**). The 2SE of this composite is well-resolved from the error envelope of the NC regression. The offset of the BSE from the NC line indicates that the Mo budget of the BSE was not solely NC in composition. As this composition falls between the CC and NC groups, one possible interpretation is that the BSE contains a modest (20 to 25 %) proportion of *r*- and *p*-process enriched CC material (**Fig. 2**). This is in contrast to the Ru isotopic composition of the BSE which shows no evidence of a CC component, based on current data for terrestrial rocks (**Fig. 1**).

Conclusions A 20 to 25 % addition of CC material to Earth during late-stage accretion lends support to the hypothesis that water was delivered to Earth predominantly through the "wet accretion" of the final major building blocks added to Earth. The corresponding Ru isotope data indicate that the last vestiges of major planetary accretion following formation of the Moon and final terrestrial core segregation did not contribute substantial water to the BSE, nor likely the lunar mantle.

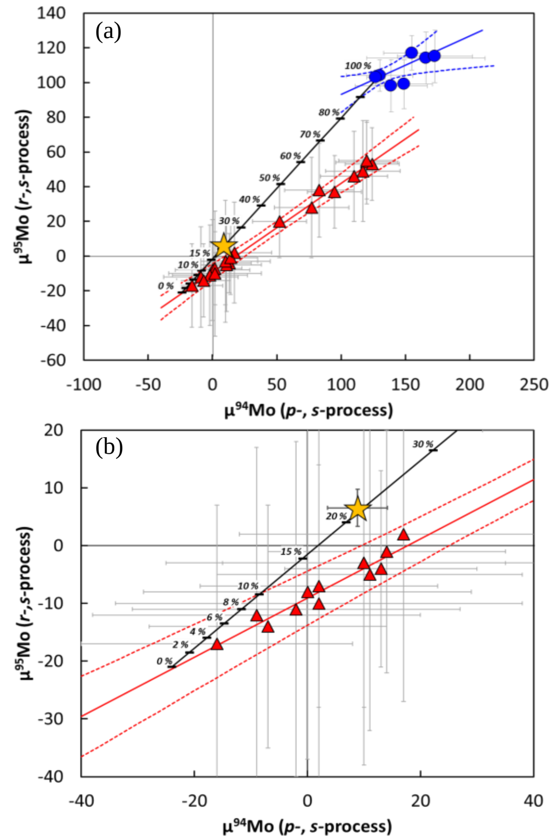

Fig. 2. μ^{94}Mo and μ^{95}Mo isotope compositions of NC iron meteorites (red), CC iron meteorites (blue), and current estimate of BSE (yellow star). Fig. 2b is a magnification of the area around the origin in Fig. 2a.

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